Consommation et Corporations Canada
Bureau des brevets
Ottawa, Canada
K1A 0C9

Consumer and Corporate Affairs Canada
Patent Office

(11) (C) 1,285,110
(21) 538,271
(22) 1987/05/28
(45) 1991/06/25
(52) 15-109

(51) Int.Cl.[5] A46B-9/00

(19)(CA) CANADIAN PATENT (12)

(54) Dental Hygiene Device

(72) Nakagawa, Yoshinori , Japan

(73) Shiken, Ltd. , Japan

(57) 14 Claims

Canada

The present invention relates to a dental hygiene device, as it were, or a photoelectric chemical reaction type capable of providing a dental hygiene effect through an oxidation-reduction reaction caused when light energy is converted into electric energy satisfying four conditions: light, n-type semiconductor, water and teeth.

It is known in recent years that fluorine is advantageously effective for teeth; thus, some tooth pastes contain this fluorine.

However, the surface of teeth, as being in contact with sputum having a lower pH value than tooth tissue, has characteristics preventing permeation of anions such as the fluorine, thereby suppressing the effect of the anions.

Accordingly, there has been provided a method in which a battery or a general electric power source is used and a negative electrode is provided at a portion of a tooth brush implanting a brush while gum is used as a positive electrode while using the human body as conductive means whereby an electrolytic reaction as expressed by the following formula is caused through sputum or drinking water.

$$H_2O \longrightarrow 1/2\ O_2 + H^+ + 2e^- \quad \text{(positive electrode)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad \text{(negative electrode)}$$

thus;

$$H_2O \longrightarrow 1/2\ O_2 + H_2$$

Thus, the permeating of the anions such as fluorine into the tooth tissue is promoted.

However, in the case of this method, since the human

body having considerable electric resistance is used as a portion of circuit, relatively large electric power is necessary for causing the above reaction. There is also another disadvantage that the electric current needed for the reaction often fails to flow due to a difference in reistance depending on the individual. If a high voltage is employed for overcoming the above difficulty, there occurs human health hazard.

The present invention provides a dental hygiene device which overcomes the aforementioned prior-art disadvantages and which is capable of effectively contributing to improved dental hygiene preventing decalcification of teeth due to decrease in pH value and preventing tooth cavity or pyorrhea through decomposition of dental plaque or deposited pigment.

According to the invention, the dental hygiene device comprises a body including an inserting portion to be inserted into the mouth and placed to react with water and/or sputum and a grip portion to be exposed out of the mouth and an n-type semiconductor accommodated in the body and adapted for causing photocatalyst reaction as at least a portion thereof is inserted into the mouth to come into contact with water and/or sputum, the n-type semiconductor being formed as a thin layer on a surface of a conductive member. ~~Suitably said~~ Said thin layer n-type semiconductor formed on the surface of the conductive member has a thickness ~~smaller~~ less than 1 μm.

Preferably said n-type semiconductor is obtained as semiconductor powder used as a raw material therefore is treated by a method selected from the group including a pressure moulding, sintering, CVD, vacuum deposition, sputtering and ion plating. Preferably said inserting portion is formed separately from said grip portion so as to be detachable from the same. Suitably said n-type semiconductor has a leading edge thereof toward said inserting portion disposed adjacent a brush provided at said inserting portion.

What the present invention essentially differs from the prior art is as follows. In contrast to the prior-art in which a high voltage is needed for causing the oxidation-reduction reaction, according to the present invention, since the semiconductor is employed for causing the photoelectric chemical reaction, an advantageous effect may be obtained even without using electric power. The present invention is also advantageous, as particularly described later, in that even in the case of using electric power in combination a sufficient effect may be obtained with a low voltage which does not pose whatever human health hazard.

In this specification, it is to be noted, the oxidation means removal of electron from a certain matter and reduction means acceptance of electron.

The present invention provides a dental hygiene device, comprising: a body having an inserting portion disposed to be inserted into a mouth and to respond to water and/or sputum; and an n-type semiconductor accommodated in said body and adapted for causing a photoelectric chemical reaction as being at least partially inserted into the mouth to come into contact with the water and/or sputum; a direct current source disposed in said body and connected to said semiconductor; and a good conductor disposed in said body and connected to said semiconductor; wherein, as said inserting portion is inserted into the mouth, said n-type semiconductor, said direct current source and said good conductor act together with to constitute a circuitry. Suitably said good conductor comprises a metal having a good corrosion resistivity. Preferably said metal having a good corrosion resistivity is selected from the group including stainless steel, Ti, Ti alloy, Al alloy, precious metals and precious metal alloys. Suitably said n-type semiconductor is selected from the group including TiO_2, ZrO_2, Fe_2O_3. Desirably said n-type semiconductor is selected from the group including TiO_2, ZrO_2, Fe_2O_3.

The present invention will be described in greater detail hereinafter with reference to the accompanying drawings in which:

Fig. 1 is a partially cutout front view showing one embodiment of a dental hygiene device related to the present invention,

Fig. 2 is a view illustrating the principle of the dental hygiene device related to the present invention,

Fig. 3(a) and Fig. 3(b) are respectively a partially cutout front view showing another embodiment of the dental hygiene device related to the present invention and a vertical section of the device shown in Fig. 3(a),

Fig. 4 is a view illustrating the principle of the dental hygiene device related to the present invention,

Fig. 5 is a partially cutout front view showing still another embodiment of the apparatus related to the present invention,

Fig. 6 is a partially cutout front view showing a further embodiment of the device related to the present invention, and

Fig. 7 is a partially cutout front view showing a still further embodiment of the dental hygiene device related to the present invention.

As shown in Fig. 2, when light strikes the n-type semiconductor 4 exposed from the mouth, the n-type semiconductor acts as photocatalyst to cause a photoelectric chemical reaction. More particularly, when the n-type semiconductor 4 formed on a surface of a conductive member is exposed to the solution, a

difference between a Fermi level of the n-type semiconductor and oxidation-reduction electric potential of the solution results in a formation of Schottky barrier on the surface of the n-type semiconductor, causing inwardly of the semiconductor a potential gradient, i.e. a deflection of band, whereby a space-charge layer is formed. If light ($h\nu$) is illuminated thereon, electron of valence band is excited into a conduction band thereby forming a positively charged hole p^+ in the balence band and excited electron e^- in the conduction band, whereby

there occurs an oxidation reaction on the illuminated surface in which the electron is removed from a substance in the solution. For example, on the surface of the semiconductor, electron is removed from H_2O molecule thereby generating a highly active OH radical. This OH radical is capable of decomposing organic acid such as lactic acid which is conceived to be direct cause of dental plaque leading to pyorrhea or of decalcification of tooth and the radical is also capable of eliminating deposited pigment.

On the other hand, the excited electron e^- in the conduction band is moved by the potential gradient of the space-charge layer into the semiconductor body and then proceeds to a back thereof (a vicinity of teeth) whereby there occurs a reduction reaction for supplying electron to the substance in the solution, thus contributing to the oral hygiene. This reaction is, for example, production of H_2 with disappearence of H^+. In this case, to be more specific, the n-type semiconductor 4 is formed as a thin n-type semiconductor layer 4a on a conductive member 4b formed of metal and the like. Accordingly, the excited electron in the conduction band moves inside the conductive member 4b before disappearing as being re-combined with the hole in the valence band inside the semiconductor body, thus the reduction reaction

for supplying the electron to the substance in the solution is caused efficiently. It is to be noted here that the semiconductor layer 4a on the surface of the conductive member 4b should be as thin as possible, preferably as thin as 1 μm because of the following reason. If the semiconductor layer 4a has a short thickness, it is possible to form substantially flat the Schottkey barrier to be formed on an outer surface of this layer 4a whereby it becomes easier to supply the electron to the substance in the solution and consequently the efficiency of the reduction reaction may be enhanced.

Also, it is conceivable to form the dental hygiene device not only of the n-type semiconductor attached to the body but also of a direct current power source and of a good conductor, these as a whole acting as a circuit when inserted into the mouth to become active.

Because of the difference between the oxidation-reduction electric potential of the solution and the fermi-level of the n-type semiconductor, there is formed the Schottkey barrier on the surface of the n-type semiconductor, causing the potential gradient, i.e. the deflection of band inwardly of the semiconductor body, whereby the space-charge layer is formed maintaining energy equilibrium. In this

condition, if light is illuminated thereon, as shown in Fig. 4, the light excitation causes an excited electron e^- in the conduction band and a hole p^+ in the valence band. This excited electron e^- moves into the semiconductor, then further into a metal 'B' and finally reaches a tooth 'D' by way of a human body, causing a reduction reaction on a surface of the tooth 'D'. For instance, the electron having reached the tooth 'D' reduces H^+ leading to decalcification of the tooth thereby to generate H_2. This means that it is possible to neutralize pH lowered by dental plaque attached to the tooth thereby advantageously preventing the decalcification of tooth resulting from a decrease in pH value. In this way, a circuit is formed having as its opposite electrode the tooth 'D' by way of the human body 'C'.

On the other hand, the hole p^+ caused in the valence band gets electron from the water in the solution thereby causing an oxidation reaction. For example, on the surface of the semiconductor, the hole p^+ gets electron to produce highly active OH radical. This OH radical is capable of decomposing organic acid such as lactic acid which is conceived to be direct cause of dental plaque leading to pyorrhea or of decalcification of tooth and the radical is also capable of eliminating deposited pigment. Such effect

is also conspicuous for S. mutans which is conceived to be bacteria responsible for tooth cavity, thereby very effectively carrying out on the whole prevention of tooth cavity or pyorrhea and beautification of tooth. In this case, it is to be noted, if the n-type semiconductor is constituted by substances such as TiO_2 and is not connected to the direct current source, the energy level in the valence band is considerably positive providing strong oxidation effect; however, since the energy level in the conduction band is not so negative, the reaction efficiency is not so high. According to the present invention, however, since the n-type semiconductor is connected to the direct current source, the energy level in the conduction band may be sufficiently negative. As a result, it is possible to promote the oxidation-reduction reaction thereby to enhance the efficiency of the photoelectric chemical reaction. That is to say, the connection of the semiconductor to the direct current source serves to promote the reduction reaction on the tooth surface and as a result to further enhance the oxidation reaction of the semiconductor.

As described above, the combination of the metal 'B' in ohmic contact with the semiconductor and the direct current source 5 helps to promote the oxidation-reduction reaction in the mouth. Therefore,

compared with the conventional dental hygiene device using a battery and the like, a high voltage source which may be detrimental for human health is not necessary.

In this case, it is to be noted, the n-type semiconductor need not necessarily be formed as the thin layer shown in Fig. 2.

The light needed for exciting the n-type semiconductor in this invention comprises natural light such as sun light or artificial light such as electric light. Therefore, the dental hygiene device according to the present invention is capable of effectively preventing tooth cavity, pyorrhea and the like without providing any detrimental effects for the human body.

Preferred embodiments of a dental hygiene device will now be particularly described with reference to the accompanying drawings.

As shown in Fig. 1, a tooth brush body 3 formed in general of synthetic resin and the like is essentially constituted by an inserting portion partially implanted with brush 1a and by a grip

portion 2 to be exposed out of the mouth. Inside the body 3, there is insertedly provided an n-type semiconductor 4 of a narrow width extending from the insertion portion 1 to the grip portion 2, a thin semiconductor layer 4a being formed on a surface of the n-type semiconductor 4. The width of this n-type semiconductor 4 should be so predetermined as to permit the semiconductor 4 to be accommodated in the body 3 and in this ~~embodiment~~ any embodiment the semiconductor 4 has a linear configuration having a width of approximately 3 mm. The n-type semiconductor 4 may also have a narrow strip configuration. The n-type semiconductor 4 used in this embodiment was formed by red-heating at 1200 to 1500°C for one or two minutes a Ti having a bar like shape with its diameter 3 mm and its length 50 mm and having a purity of 99.4 %, thereby producing TiO_2.

Figs. 3(a) and 3(b) show a tooth brush as another embodiment of the dental hygiene device related to the present invention. This tooth brush also includes an n-type semiconductor providing photoelectric effect. This n-type semiconductor 4 has its one end connected to a metal Ti as a good conductor 6 ohmic-contactable with the semiconductor. Between the good conductor 6 and the semiconductor, there is inserted a battery acting as a direct current source 5.

Further, inside the body 3 of the dental hygiene device shown in Fig. 1 and Figs. 3(a) and 3(b), there is formed a groove for catching water. And, the photoelectric chemical reaction is effectively promoted through the water deposited in the groove 7. In the case the semiconductor 4 is formed transparent, substantially the whole of the semiconductor 4 may be inserted into the mouth with only a side portion thereof being exposed to the outside. Further, it is also possible to dispose a side leading edge of the inserting portion 1 of the semiconductor 4 shifted from the position shown in Fig. 1 and Fig. 3(a) toward the vicinity of the brush 1a. With this arrangement, the photoelectric chemical reaction of the semiconductor 4 acts more effectively on the teeth.

The semiconductor 4 may be constituted, in addition to TiO_2, also by ZrO_x Fe_2O_3 and the like. In short, any semiconductor may be used which is capable of producing sufficient photoelectric current in response even to natural light. Also, the semiconductor may be formed in any other fashion than that described hereinbefore. For example, powdered Ti, Zr, Fe and the like is sintered at a high temperature or plate-shaped Ti, Zr, Fe and the like is treated by electrolytic oxidation, thereby producing TiO_2, ZrO_2, Fe_2O_3, respectively. Still further, powder

semiconductor used as a raw material may directly undergo pressure moulding or sintering process, or a semiconductor layer may be formed on an appropriate base plate by a CVD method, a vacuum deposition method, a sputtering method, an ion plating method and the like.

On the other hand, if the surface of the semiconductor bears a metal which is a good conductor, it becomes easier to cause the reduction reaction on the surface of the semiconductor. Especially if a precious metal such as Pt is employed as the metal borne on the surface, the metal acts like a catalysis in response to generation of hydrogen to increase the effect in the mouth. Also, even if any other metal than Pt such as Pd, Au, Ag or a combination thereof or Ti or Ti alloy and the like is employed, the effect is enhanced compared with the case when the semiconductor alone is employed.

The good conductor 6 may comprise, in addition to Ti, various kinds of stainless steel, Al alloy, Ag and Ag alloy and others.

The configuration of the body 3 may be conveniently modified; thus, the present invention is not limited by the one shown in the accompanying drawings. For example, in the case of the body 3 shown in Fig. 1 and in Fig. 3(a), the brush 1a may not

be needed. In this case, the teeth are washed, e.g. by washing liquid jetted from a portion of the body.

Fig. 5 shows a tooth brush as another embodiment of the dental hygiene device related to the present invention. In the case of this tooth brush, a compact semiconductor 14 is attached to the grip portion 2 and a conductive line 8 is extended therefrom to the inserting portion 1, thereby forming a conductive passage.

Fig. 6 shows a tooth brush as still another embodiment of the dental hygiene device related to the present invention. This tooth brush has a water-depositing groove 9 in place of the conductive line 8 shown in Fig. 5.

Fig. 7 shows a tooth brush as a further embodiment of the dental hygiene device related to the present invention. In this case, a body 13 is used as a conductive passage as being formed of a conductive material(unharmful for the human body).

Figs. 5 through 7 show embodiments of the dental hygiene device having a semiconductor, a direct current source and a conductive member. In place of these, the device may have a thin layer type semiconductor without using the direct current source.

Further, the inserting portion 1 may be formed separately from the grip portion such that the

inserting portion 1 may be detachable from the latter. With this arrangement, even if the brush 1a implanted in the inserting portion 1 may wear due to use, the tooth brush may be repeatedly used by replacing only the inserting portion 1 without throwing away the whole tooth brush. In addition to this economic merit, this arrangement may provide another advantage of convenience since it becomes easier to clean the surface of the semiconductor.

538271

ABSTRACT OF THE DISCLOSURE

A dental hygiene device having a body with an inserting portion disposed to be inserted into a mouth and to respond to water and/or sputum and an n-type semiconductor accommodated in the body and adapted for causing a photocatalyst reaction as being at least partially inserted into the mouth to come into contact with the water and/or sputum, the n-type semiconductor being formed as a thin layer on a surface of a conductive member. And, a dental hygiene device having a body with an inserting portion disposed to be inserted into a mouth and to respond to water and/or sputum and an n-type semiconductor accommodated in the body and adapted for causing a photoelectric chemical reaction as being at least partially inserted into the mouth to come into contact with the water and/or sputum, a direct current source disposed in the body and connected to the semiconductor and a good conductor disposed in the body and connected to the semiconductor. As the inserting portion is inserted into the mouth, the n-type semiconductor, the direct current source and the good conductor act togetherwith to constitute a circuitry.

1285110

3-1

Fig.1

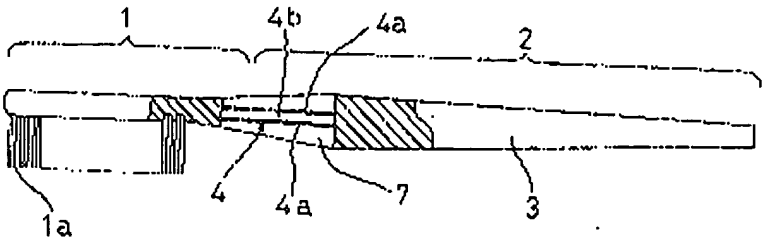
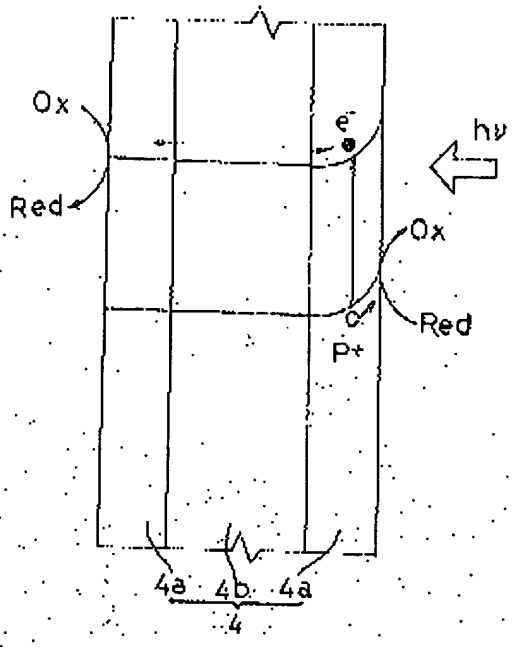


Fig.2



Ridout & Clerk

1285110

3-2

Fig.3(a)

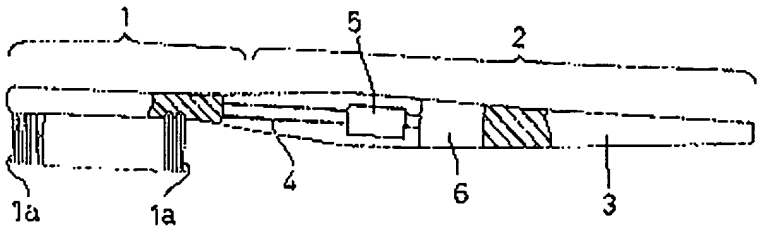
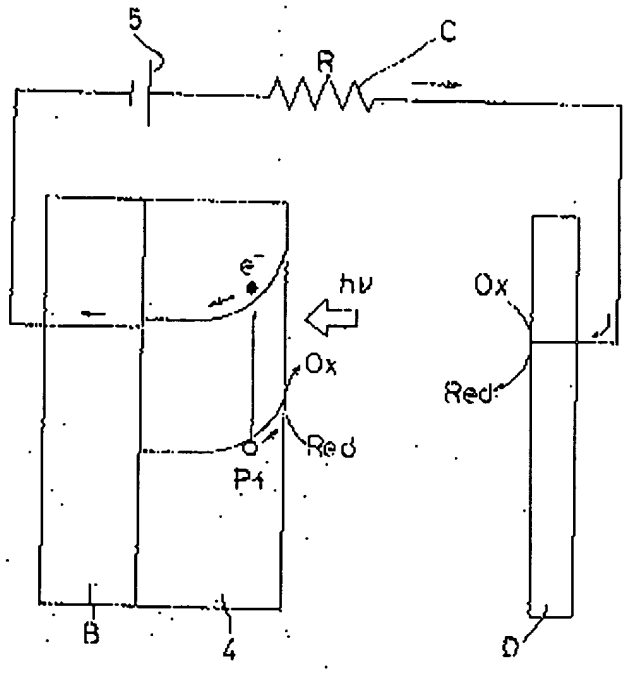


Fig.3(b)

Fig.4



1285110

3-3

Fig.5

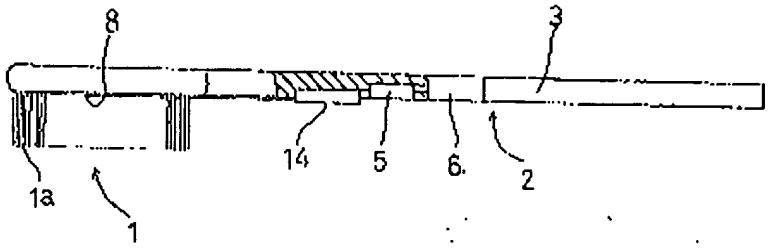


Fig.6

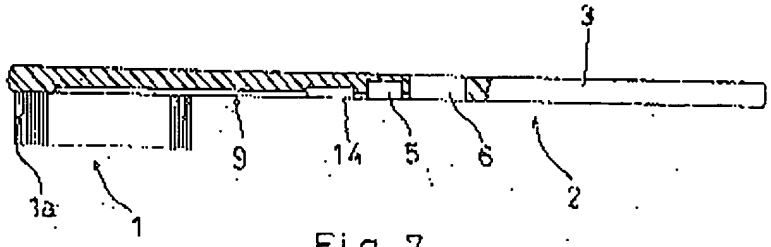
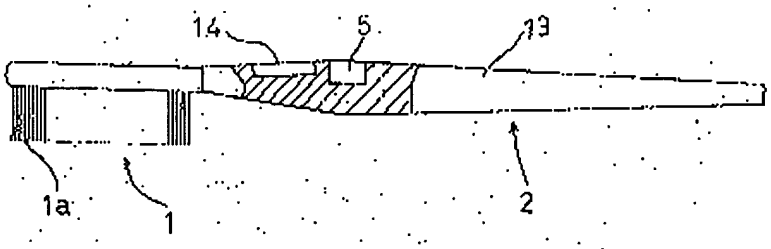


Fig.7



Ridout & Maybee

1285110

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A dental hygiene device, comprising: a body having an inserting portion disposed to be inserted into a mouth and to respond to water and/or sputum; and an n-type semiconductor accommodated in said body and adapted for causing a photocatalyst reaction as being at least partially inserted into the mouth to come into contact with the water and/or sputum; said n-type semiconductor being formed as a thin layer having a thickness less than 1 μm on a surface of a conductive member.

2. A dental hygiene device, comprising: a body having an inserting portion disposed to be inserted into a mouth and to respond to water and/or sputum; and an n-type semiconductor accommodated in said body and adapted for causing a photoelectric chemical reaction as being at least partially inserted into the mouth to come into contact with the water and/or sputum said n-type semiconductor being formed as a thin layer having a thickness less than 1 μm on a surface of a conductive member; a direct current source disposed in said body and connected to said semiconductor; and a good conductor disposed in said body and connected to said semiconductor; wherein, as said inserting portion is inserted into the mouth, said n-type semiconductor, said direct current source and said good conductor act together to constitute a circuitry.

3. A dental hygiene device, as claimed in claim 2, wherein said good conductor comprises a metal having a good corrosion resistivity.

4. A dental hygiene device, as claimed in claim 3, wherein said metal having a good corrosion resitivity is selected

from the group including stainless steel, Ti, Ti alloy, Al alloy, precious metals and precious metal alloys.

5. A dental hygiene device, as claimed in claim 1, wherein said n-type semiconductor is selected from the group including TiO_2, ZrO_2, Fe_2O_3.

6. A dental hygiene device, as claimed in claim 2, wherein said n-type semiconductor is selected from the group including TiO_2, ZrO_2, Fe_2O_3.

7. A dental hygiene device, as claimed in claim 5 or 6, wherein said n-type semiconductor bears Pt on a surface thereof.

8. A dental hygiene device, as claimed in claim 5 or 6 wherein said n-type semiconductor bears on a surface thereof any one selected from the group including Ti alloy, any other precious metals than Pt or alloys formed thereof.

9. A dental hygiene device, as claimed in claim 5, wherein said n-type semiconductor selected from the group including TiO_2, ZrO_2 and Fe_2O_3 is formed by sintering at a high temperature Ti, Zr and Fe in the form of powder, respectively.

10. A dental hygiene device, as claimed in claim 9, wherein said TiO_2 is obtained by red-heating Ti at a temperature between 1200 to 1500°C for 2 to 10 minutes.

11. A dental hygiene device, as claimed in claim 5 or 6, wherein said n-type semiconductor selected from the group including TiO_2, ZrO_2 and Fe_2O_3 is obtained by an electrolytic oxidation of Ti, Zr, and Fe, respectively.

12. A dental hygiene device, as claimed in claim 1 or 2, wherein said n-type semiconductor is obtained as semiconductor powder used as a raw material therefore is treated by a method selected from the group including a pressure moulding, sintering, CVD, vacuum deposition, sputtering and ion plating.

13. A dental hygiene device, as claimed in claim 1 or 2, wherein said inserting portion is formed separately from said grip portion so as to be detachable from the same.

14. A dental hygiene device, as claimed in claim 1 or 2, wherein said n-type semiconductor has a leading edge thereof toward said inserting portion disposed adjacent a brush provided at said inserting portion.

This Page is inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.
As rescanning documents *will not* correct images problems checked, please do not report the problems to the IFW Image Problem Mailbox